

SULPHUR BLACKENING OF CAN INTERIORS D 18
 AS INFLUENCED BY THE SEVERITY OF BEEF PROCESSING
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It is generally belived, that sulphide stain on tinsplate develops mainly during the period of processing the filled cans at high temperature and may continue to grow slowly during subsequent storage at ordinary temperatures (Hoare et al.,1965).

However, any quantitative evidence regarding the extent to which the sulphur blackening of can interiors occurs, with regard to the severity of processing and storage conditions is lacking. The reported study has been made in order to elucidate these relationships.

EXPERIMENTAL

The tinsplate for containers

Non-lacquered tinsplate 99 x 63 mm round cans were used. Bodies and ends were made from 0.28 mm hot-dipped tinsplate, with the following characteristics:

coating weight	35.5 g/m ²
"Thiocyanate Value"	0.168 mg of
(Hoare and Britton,1962)	iron per square decimeter
The Iron Solution Value	54 micrograms
(Hoare and Britton,1962)	of iron per square decimeter

Outline of processing and storage procedure

Tins of beef "in jelly" type were prepared. The fresh raw beef meat was taken from the round of cows about 4-5 years old. It was stored four days after slaughtering at 2-4°C. The pH of raw meat was 5.8, fat content about 2.2% and protein content (Nx6,25) 18.8%.

Each can was packed to about 430 g net weight. The filling had the following formula:

beef meat, cut into cubes of about 3 cm	360 g
connective tissues constituents, comminuted	10 g
gelatin of high quality	10 g
pork fat (lard), incl. small amounts of several spices	13 g
salt	7,2 g
distilled water	30 g

The stationary heat sterilization was affected at 121°C and 115°C using the small laboratory retort (De Vilbriss, U.S.A.) packed with 12-14 cans, and filled with water. All cans were water-cooled until a temperature of 40°C inside was reached.

To record the heat penetration, the NiCr-Constantan thermocouple needles were inserted radially at the geometrical centre of two cans tested (Foster Instrument Co., Ltd, England). The sterilization values (F_{oc}) were controlled during heating using a numerical variant of the improved general method (Patashnik, 1953). On that way nearly equal sterilization values at both temperatures were achieved, as given in Table 1.

After sterilization, the canned samples were divided into three separate parts A, B and C, being stored before opening for 24 hrs. at 5°C, 28 days at 35°C and the same period at 55°C respectively.

Quantitation of a sulphide film on a tinplate

The degree of sulphide staining is usually determined by visual examination of the cans and therefore satisfactory precision is not possible.

The author developed for the purpose a special experimental technique, called the Leucometer Test. Details of this technique

will be published elsewhere. In brief, test specimens of the tinplate from the same batch as the cans investigated, with the edges protected in melted tin, were introduced inside the meat filling, being examined in chosen period after processing. Using 99 x 63 mm cans, two test samples of the size 50 x 50 mm were placed inside, the Leucometer Value (LV), expressed in per cent of absolute whiteness was then measured with Zeiss's Leucometer. Magnesium oxide (87.41 LV) served as a standard.

Two readings for each side of the test specimen were recorded and each group investigated included four cans, thus giving 32 readings per one group. All comparisons were made using the calculated average values.

Even for most heavy stained samples, the coefficient of variation was only 2.9%.

A good correlation has been obtained between instrument readings with test specimens and six visual panels score, the correlation coefficient, r , ranging from 0.70 to 0.81 for 25 different groups of cans taken from this study. Judges were scoring the sulphide staining on the whole inner surface of cans, which were prepared as flat "can patterns" to facilitate evaluation.

It was noticed, that various types of intact tinplate, even hot-dipped and electrolytic types, are similar in their LV. For example, LV of electrolytic tinplate N°75 (coating weight 16.6 g (m^2)) was 66.65 ± 1.48 as compared with 67.45 ± 1.24 for the hot-dipped tinplate (coating weight 35.5 g (m^2)).

Therefore the direct leucometer readings for stained tinplate are of more than only relative value.

Sterilization weight loss determination

According early observation of Kefford and Lynch (1941), the

production of gaseous hydrogen sulphide is not a stage in the formation of sulphide stains, but blackening of can interior is under the action of sulphide ions in the liquid. For that reason the sterilization weight loss, which is, especially for low-fat pieces of meat, largely water, was determined for each group of canned samples.

Meat parts (about 370 g) were weighed before cans' filling and then after sterilization (as drain weight), the weight loss being computed as per cent of the fresh meat part.

Statistics

The differences found in the experiments were statistically calculated using Tukey's simplified procedure, as described by Mahoney et al. (1957). The regression equation were computed from mean values obtained.

RESULTS AND DISCUSSION

Sulphur blackening within each of experimental group

The differences found between the sulphide effect of the canned beef of equal F_{oc} at two temperatures might be rather neglected (Table 2).

The differences between A, B and C storage types for each processing temperature, compared with the former storage type (type A being compared with the intact tinplate) were all significant at the 0.01 P level.

Sulphur blackening as influenced by the sterilization value

Only very significantly differences within each of storage conditions were found, when the experimental groups were compared with the former sterilization value effect on LV.

Average values of LV obtained are plotted against F_{oc} at Fig.1.

As discussed before, the hyperbolic functions found are independent, in fact, of the processing temperature for the equal sterilization values. The storage of canned beef resulted in slightly but progressive staining of can interiors.

Sulphur blackening versus sterilization weight loss of meat

The sterilization weight losses measured soon after processing (samples type A) for each of the experimental group and processing temperature, are given in Table 3.

In similarity to sulphide staining changes, weight losses for the both processing temperatures are also quite similar within each of experimental group.

When the LV measurements are plotted against these sterilization weight losses of the range observed, a linear correlation is found for each type of storage, independently of processing temperature (Fig.2.).

In other words, after initial rapid staining as a result of a considerable drip loss connected with a mild heat treatment only ($F_{oc} 3$), the further sulphide staining was found to be true linear function of the sterilization weight loss.

The following correlation coefficients, r , and appropriate regression lines were found to be valid, being computed for each eight groups of samples in the range of 30 - 50% weight loss (X):

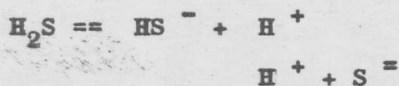
storage type	r	regression line
A	- 0.93	$LV = 80.29 - 0.73 X$
B	- 0.95	$LV = 74.48 - 0.73 X$
C	- 0.95	$LV = 76.63 - 0.73 X$

According to the "rule of thumb" that corrosion reaction rate in plane cans is doubled for every 10°C rise in storage temperature (Koehler and Canonico, 1957), the storage conditions B and C

(28 days at 35°C and 55°C) may be considered as equal to 4 and 14 months at 15°C respectively.

From the results obtained the sulphide staining of can interiors depends of the liquor content of the canned product, existing during sterilization, as the result of the product formula and the severity of processing, effecting drip loss from the meat.

It may be concluded, that the liquor content of the can filling (or, for the given product, sterilization weight loss) reflects closely the amount of the sulphide ions,



responsible for the formation of sulphides on the surface of tinplate.

For the type of product studied, only slightly but gradually blackening of the can interiors took place. Since Parr and Levett (1969) observed that hydrogen sulphide in cooked chicken meat disappeared rapidly after cooking, even in nitrogen atmosphere, and the author (Ziemba, 1970) indicated the interaction between hydrogen sulphide and ammonia in canned beef, a slow rate of sulphur staining on storage is confirmed with these findings.

The direct influence of sterilization loss on the sulphide blackening of can interiors was recently confirmed in our laboratory with a comminuted canned beef product.

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A c k n o w l e d g e m e n t

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Table 1. The sterilization value of thermal processes, F_{oc} .*)

Processing temperature	Experimental group			
	I	II	III	IV
115°C	1.91	6.33	13.76	30.49
121°C	3.04	5.95	13.81	31.46

*) maximal value found.

Table 2. Changes in sulphide staining of can interiors (4 cans tested) as LV : statistical significance of differences between samples processed to equal F_{oc} value at 115°C and 121°C within each of experimental group.

Experimental group	P level		
	Storage conditions type		
	A	B	C
I	0.05	NOT	0.01
II	NOT	NOT	0.01
III	0.05	0.01	0.01
IV	0.01	0.05	0.05

A - 24 hrs. at 5°C, B - 28 days at 35°C, C - 28 days at 55°C

Table 3. The sterilization weight loss of canned beef, %.
(averages of duplicated determinations for A type samples)

Processing temperature	Experimental group			
	I	II	III	IV
115°C	29.7	34.9	41.2	45.9
121°C	28.4	32.6	39.9	45.9

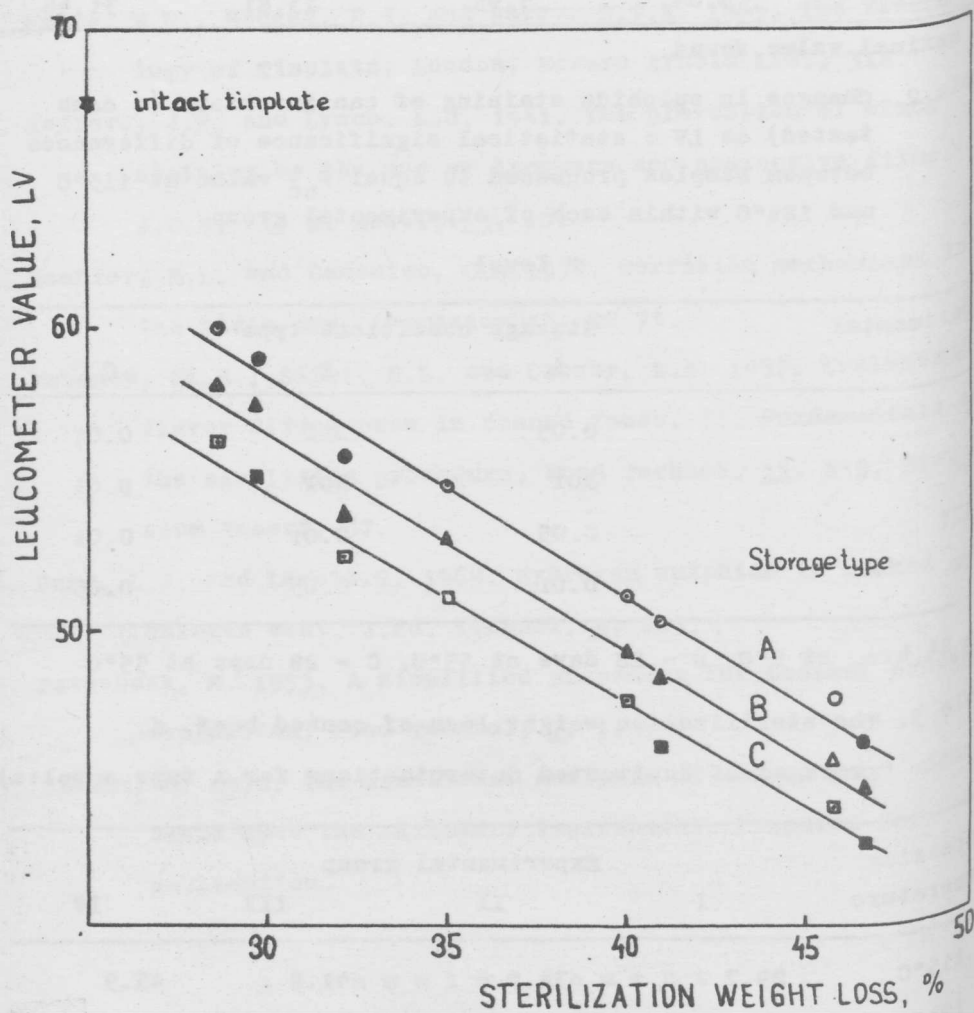


Fig.1. Relationship between sulphur staining of can interiors (expressed as LV) and sterilization value of canned beef (points for samples processed at 115°C made dark).

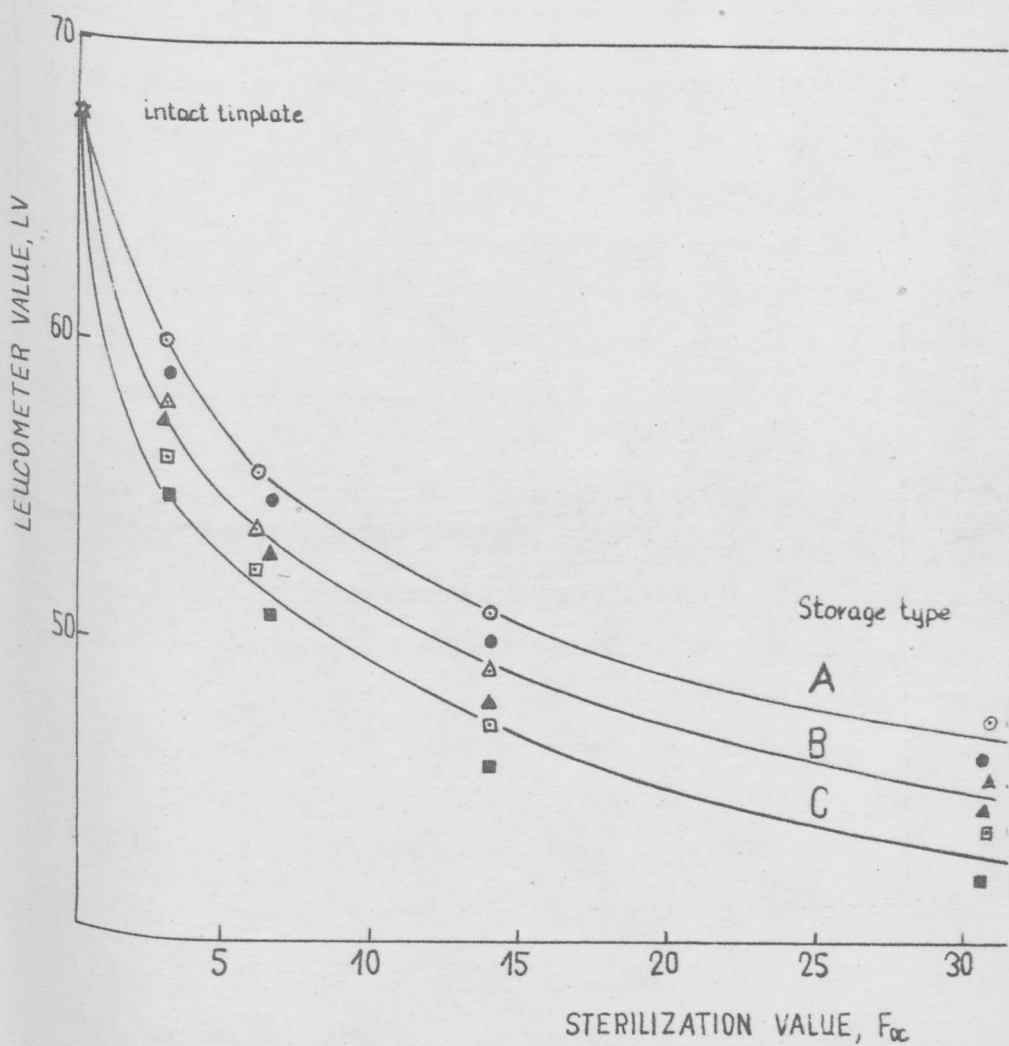


Fig. 2. Regression between sulphur staining of can interiors (expressed as LV) and the sterilization weight loss of canned beef (points for samples processed at 115°C made dark).